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On STUDIES ON THE SYNTHESIS OF BORON HYDRIDE SYSTEMS

For the period July 1, 1981 - May 31, 1982

Submitted by Sheldon G. Shore
Department of Chemistry

Date July 30, 1982

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Syntheses of the new anion $[BH_3Cl]^-$, B_2H_6 , $B_{10}H_{14}$, and 2- BrB_4H_9 are discussed. The use of B_5H_9 as a starting point in the preparation of $B_9H_{13}L$, $B_{10}H_{12}L_2$ and nido-5,6-RR'C ₂ B ₈ H ₁₀ is described.		

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Forward

This report covers the period July 1, 1981 - May 31, 1982. In the time frame cited above we have been concerned with several aspects of Studies on the Syntheses of Boron Hydride Systems. The work described here is an extension of the program which is discussed in an earlier final report: November 1981 No. 761119/711144 for Grant No. DAAG 29-78-G-0112.

In this report we describe the new anion $[\text{BH}_3\text{Cl}]^-$ and how it is employed to improve the yield of $\text{B}_{10}\text{H}_{14}$ in our "one pot" procedure for preparing $\text{B}_{10}\text{H}_{14}$ from B_5H_9 .

Dry syntheses of B_2H_6 and $\text{B}_2\text{H}_5\text{Br}$ are described and the preparation of $2\text{-BrB}_4\text{H}_9$ is considered in several solvents.

Our "one pot" syntheses of higher borane systems have been extended to include several thioether derivatives of the type $\text{B}_9\text{H}_{13}\text{L}$ and bis-ligand derivatives $\text{B}_{10}\text{H}_{12}(\text{P}\phi_3)_2$ and $\text{B}_{10}\text{H}_{12}(\text{SEt}_2)_2$. New preparations of carboranes of the type nido-5,6-R,R'C₂B₈H₁₀ are discussed.

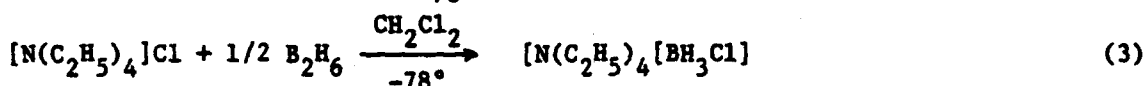
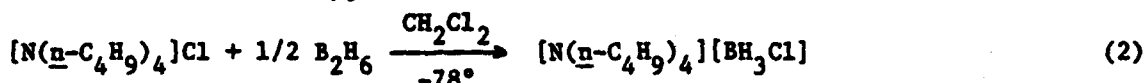
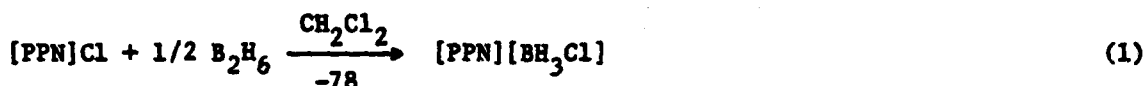


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Results and Discussion

1. Preparation and Characterization of the $[\text{BH}_3\text{Cl}]^-$ Ion.

From tensimetric titrations we have demonstrated the formation of the $[\text{BH}_3\text{Cl}]^-$ ion.



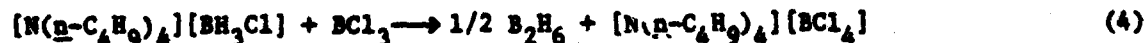
Under similar reaction conditions there is no evidence for the formation of the analogous ions $[\text{BH}_3\text{Br}]^-$ and $[\text{BH}_3\text{I}]^-$.

The salts $[\text{PPN}][\text{BH}_3\text{Cl}]$, $[\text{N}(\underline{\text{n-C}_4\text{H}_9})_4][\text{BH}_3\text{Cl}]$, and $[\text{N}(\text{C}_2\text{H}_5)_4][\text{BH}_3\text{Cl}]$ readily disproportionate in CH_2Cl_2 solution at room temperature to give $[\text{B}_2\text{H}_7]^-$, $[\text{BH}_2\text{Cl}_2]^-$ and $[\text{BH}_4]^-$. However in the solid state these salts appear to be stable at room temperature for extended periods of time in the absence of air.

In collaboration with Dr. J. C. Huffman at the Indiana University Molecular Structure Center and Dr. Robert Bau of the University of Southern California, the crystal and molecular structure of $[\text{PPN}][\text{BH}_3\text{Cl}]$ has been determined. The $[\text{BH}_3\text{Cl}]^-$ ion is tetrahedral and the B-Cl distance is the longest observed (2.01Å). This of course suggests a weak bond and suggests that the anion might prove to be a ready source of BH_3 . This point is elaborated on below.

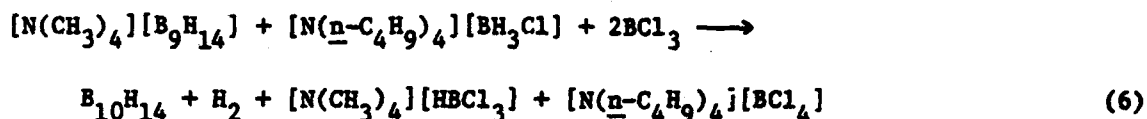
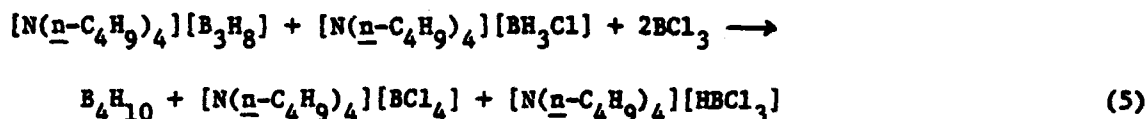
2. Addition of BH_3 to B_3H_7 and B_9H_{13} via the Anion $[\text{BH}_3\text{Cl}]^-$.

The reaction of $[\text{N}(\underline{\text{n-C}_4\text{H}_9})_4][\text{BH}_3\text{Cl}]$ with BCl_3 results in the abstraction of Cl^- to give 80-90% yields of B_2H_6 . This result suggested the possibility of using



$[\text{BH}_3\text{Cl}]^-$ as an external BH_3 source for polyhedral expansion in the absence of a solvent, rather than relying on BH_3 transfer as previously described in our earlier report¹ and publications.^{2,3} This method would eliminate the loss of boron in the polymeric residues suggested in the previously cited material.^{1,2,3} Reactions (5) and (6) below illustrate the stoichiometries used and the proposed

results for BH_3 addition to B_3H_7 and B_9H_{13} respectively.



In the case of reaction (4), the predicted yield of B_4H_{10} is not achieved, rather two independent reactions occur to generate B_4H_{10} and B_2H_6 as previously described.^{1,2,3} However, in reaction (5) the yield of $\text{B}_{10}\text{H}_{14}$ obtained is 64% based upon the stoichiometry of the reaction. This yield is nearly 71% if based solely on the boron in $[\text{B}_9\text{H}_{14}]^-$, thus indicating that reaction (5) appears to be proceeding as proposed. In our usual preparation of $\text{B}_{10}\text{H}_{14}$ from $\text{B}_9\text{H}_{14}^-$ the yield of $\text{B}_{10}\text{H}_{14}$ cannot exceed 50% of the boron in $\text{B}_9\text{H}_{14}^-$. Additionally, the quantity of B_2H_6 isolated is far less than predicted for the independent reaction of $[\text{BH}_3\text{Cl}]^-$ with BCl_3 . Further investigations into this system resulted in no further increases in yield of $\text{B}_{10}\text{H}_{14}$ when $[\text{N}(\underline{\text{n-C}_4\text{H}_9})_4][\text{BH}_4]$ was substituted for $[\text{N}(\underline{\text{n-C}_4\text{H}_9})_4][\text{BH}_3\text{Cl}]$. Thus the addition of BH_3 to B_9H_{13} is successful to a limited extent.

3. 2-BrB₄H₉ from [B₃H₇Br]⁻

The availability of the salt $[\text{N}(\underline{\text{n-C}_4\text{H}_9})_4][\text{B}_3\text{H}_7\text{Br}]^4$ suggested the possibility of preparing the 2-bromo derivative of tetraborane(10) through hydride ion abstraction from $[\text{B}_3\text{H}_7\text{Br}]^-$ followed by BH_3 transfer.

When $[\text{N}(\underline{\text{n-C}_4\text{H}_9})_4][\text{B}_3\text{H}_7\text{Br}]$ is reacted with BBr_3 in CH_2Cl_2 at -78° , 2-BrB₄H₉ and B₄H₁₀ are isolated in 15-20% yield each. Other boron containing species isolated include 2-BrB₅H₉, B₂H₆, B₃H₉, BrB₂H₃, and 1-BrB₅H₉ (1-10% yield each). The total amount of boron in the volatile products is 60-65% of boron in $[\text{B}_3\text{H}_7\text{Br}]^-$. Since both brominated and non-brominated boranes are obtained and since the solid reaction products contain both $[\text{BBr}_4]^-$ and $[\text{HBBR}_3]^-$ it appears that both hydride ion and bromide ion are susceptible to abstraction by BBr_3 . This would result in the formation of both "B₃H₇" and "B₃H₆Br" units which could undergo polyhedral expansion by transfer of either BH_3 or BH_2Br . Additionally, some decomposition must also occur to yield the B₂ and B₃ species cited above.

Various attempts were made to increase the yield of $2\text{-BrB}_4\text{H}_9$ with respect to the other boranes produced by varying the reaction conditions. Table I summarizes the yields of B_4H_{10} and $2\text{-BrB}_4\text{H}_9$ obtained and the reaction conditions employed for pertinent reactions. Of particular interest is the observation that B_4H_{10} production is directly proportional to the number of chlorine atoms in the solvent employed. This result can be rationalized from the standpoint that the solubility of the $[\text{BBr}_4]^-$ salt decreases as a more highly chlorinated solvent is employed. This method for preparing $2\text{-BrB}_4\text{H}_9$ provides a reasonable alternative to the only other reported procedure which involved the reaction of B_4H_{10} and Br_2 at -15° for 18 hours.⁵

COMPARATIVE YIELDS OF $2\text{-BrB}_4\text{H}_9$ AND B_4H_{10}

Solvent	Temperature	B_4H_{10}	$2\text{-BrB}_4\text{H}_9$
CH_2Cl_2	-78°C	15%	15%
CHCl_3	0°C	40%	Trace
CCl_4	0°C	43%	0%

Yield is calculated from boron in $\text{B}_3\text{H}_7\text{Br}^-$.

4. Convenient, Dry Syntheses of B_2H_6 and $\text{B}_2\text{H}_5\text{Br}$.

Diborane(6) was obtained in 95% yield from the reaction of a vigorously stirred mixture of NaBH_4 and BF_3 at room temperature and 1 atm. pressure.



This synthesis of B_2H_6 differs from the traditional⁵ preparation of B_2H_6 in that an ethereal solvent is not used. Furthermore, the generation of B_2H_6 probably occurs through hydride ion abstraction to give $[\text{HBF}_3]^-$ which disproportionates to $[\text{BH}_4]^-$ and $[\text{BF}_4]^-$.

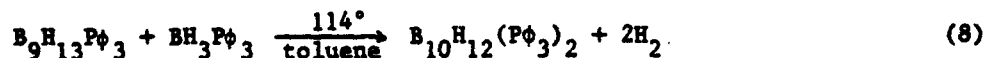
Through the reaction of LiBH_4 with BBR_3 , we have developed a simple preparation of $\text{B}_2\text{H}_5\text{Br}$ in 80% yield. With vigorous stirring of reactants, this reaction occurs at room temperature. This procedure appears to be superior to the conventional⁶ method of preparing $\text{B}_2\text{H}_5\text{Br}$ which involves the reaction of

BBr₃ with B₂H₆.

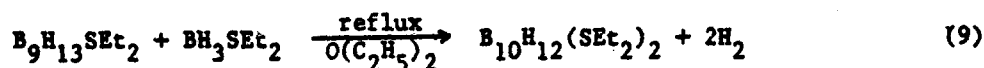
5. Preparation of B₉H₁₃L and B₁₀H₁₂L₂ Complexes using B₅H₉ as a Starting Material.

Our final report for Grant No. DAAG 29-78-G-0112 described the use of B₅H₉ as a starting material for the preparation of B₉H₁₄⁻ in 90% yield and its subsequent conversion to B₉H₁₃SEt₂ and B₉H₁₃Pφ₃ in effectively "one pot" synthetic procedures. We have extended these procedures to include the preparation of the complexes B₉H₁₃S(n-C₄H₉)₂, B₉H₁₃S(t-C₄H₉)₂, B₉H₁₃Tetrahydrothiophene, and B₆H₁₃Thiophene in yields of about 60%. Thus, we have established practical routes to adducts of the type B₉H₁₃L using B₅H₉ as a starting material.

We have achieved a 65% conversion of B₉H₁₃Pφ₃ to high quality B₁₀H₁₃(Pφ₃)₂ through the following reaction



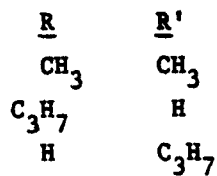
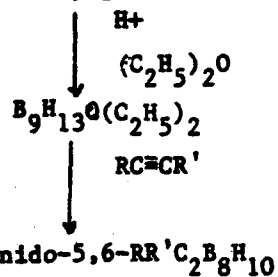
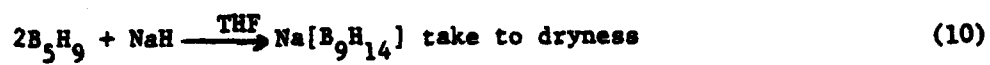
The analogous reaction shown below has also been observed giving 10-20% yield of B₉H₁₃SEt₂. Optimum conditions for conducting this reaction are currently



being studied on Grant No. DAAG-29-82-K-0112. By the same token current studies also involve conversion of B₉H₁₃S(n-C₄H₉)₂, B₉H₁₃S(t-C₄H₉)₂, B₉H₁₃Tetrahydrothiophene, and B₉H₁₃Thiophene to bis-ligand adducts: B₁₀H₁₂L₂. Our ultimate goal is to convert such materials to icosahedral carboranes.

6. Preparation of nido-5,6-R'₂C₂B₈H₁₀ Carboranes using B₅H₉ as a Starting Material.

In our final report for Grant No. DAAG-29-78-G-0112 we described a "one-pot" synthesis of nido-5,6-φ₂C₂B₈H₁₀ from B₅H₉. The preparative procedure employed the formation of B₉H₁₃SEt₂ which was then reacted with φC≡Cφ in order to form nido-5,6-φ₂C₂B₈H₁₀. We have since made significant improvements in the synthetic procedure and find that it is not necessary to go through the B₉H₁₃SEt₂ intermediate. Three carboranes have been prepared using the procedure which is outlined below and we have obtained yields of up to 37% carborane based upon boron in the B₅H₉ starting material.



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Publication

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Preparation of B_2H_6 , B_4H_{10} , B_5H_{11} , and $B_{10}H_{14}$ ", Inorg. Chem. 1982, 21, 1952.

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8